LABORATORY AND TECHNICAL PRODUCTION OF FLUORINE AND ITS COMPOUNDS

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"In my opinion the hazards of work with fluorine and its compounds have been greatly over-rated. When treated with the respect which is due to it, fluorine is just another substance." [1]

Fluorine was made on an industrial scale in the U.S.A. in the last war in simple equipment, largely of mild steel, and handled without difficulty. A large fluorine plant was operated in Germany also. Fluorine can now be made in the laboratory or in industry without difficulty, and the chemistry of fluorine can begin to overtake that of other common elements which have been readily available for many years. It is of interest to see the stages of the development of fluorine production, the problems which have been solved, and those which yet remain.

Although it is 62 years since Moissan first isolated fluorine in 1886, there was little further work done for 30 years, and developments almost as revolutionary as Moissan's first preparation may be dated from 1919, when Mathers and his co-workers[2] first used as electrolyte fused potassium acid fluoride. Between 1886 and 1919 there were only some six papers published by workers in the field of elementary fluorine, between 1919 and 1939 there were at least 25 papers giving some description of fluorine cells, as well as 9 patents, and many more papers dealing with the use of elementary fluorine.

All fluorine cells employ a potassium fluoride-hydrogen fluoride electrolyte: there are several compounds formed in this system, and Cady[3] gives the data of Table I (the tension of hydrogen fluoride is the approximate partial pressure at the melting point).

Electrolytes in three different working regions have been employed: (1) Low-temperature electrolyte, a relatively dilute solution of potassium fluoride (about KF,13HF, with less than 20% by weight of potassium

Table I

Solid phase.	KF, %	M.p.	HF tension, mm.	Solid phase.	KF, %	M.p.	HF tension, mm.
HF	nil	−83·7°		KF,2·5HF	53·8	64·3°	~55
Eutectic	17·7	−97		Eutectic	55·8	61·8	—
KF,4HF	42·1	72·0		KF,2HF	59·2	71·7	~20
Eutectic	46·3	63·6	~250	Eutectic	61·5	68·3	~15
KF,3HF	49·2	65·8	~130	KF,HF	74·4	239·0	~25
Eutectic	52·1	62·4	—	Eutectic	75·4	229·5	~15

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[1] G. H. Cady, *Ind. Eng. Chem.*, 1947, **39**, No. 3, 10A.

[2] W. L. Argo, F. C. Mathers, B. Humiston, and C. O. Anderson, *Trans. Electrochem. Soc.*, 1919, **35**, 335.

[3] *J. Amer. Chem. Soc.*, 1934, **56**, 1431.

fluoride) as used by Moissan, at subnormal temperatures. (2) High-temperature electrolyte, approximately molten KF,HF, first introduced by Mathers, working temperature about 250°. (3) Medium-temperature electrolyte, approximately molten KF,2HF, first introduced in 1925 by P. Lebeau and A. Damiens; [4] working temperature about 100°. The partial pressure of hydrogen fluoride over the low-temperature electrolyte is very high, and the fluorine produced is heavily contaminated. Over the other two electrolytes the partial pressure is very much less, and the fluorine (and hydrogen) are contaminated with 5–15% of hydrogen fluoride at the working temperature. F. C. Mathers and P. T. Stroup [5] have investigated the possibility of finding an electrolyte with lower melting point, and draw attention to the advantages of cæsium acid fluorides: owing to the low melting points, the hydrogen fluoride tension of these is negligible. Some attention to this point has also been paid by German workers.

In the low-temperature electrolyte, the corrosion of the platinum anodes which must be employed is very heavy. O. Ruff [6] indicates a current efficiency of 31% on fluorine, and a platinum loss of 5 g. per g. of fluorine (although as recently as 1932 proposals were made for a somewhat modified cell working at room temperature, claiming advantages in a nickel anode).[7] Moissan found that graphite anodes completely disintegrated almost immediately on starting electrolysis in low-temperature electrolyte, and found that platinum in high-temperature electrolyte was too rapidly corroded to be of any value. He did not examine graphite in this electrolyte, however, and it was left to Argo, Mathers, Humiston, and Anderson to show how effective this was, and to open the door to a new development in fluorine production. Medium-temperature electrolyte, using a nickel anode, was proposed by Lebeau and Damiens, for the specific reason that the formation of carbon fluorides, reputed to occur in the high-temperature cell, was avoided, and a purer fluorine obtained. This electrolyte had other advantages, however, and will probably oust all others from general use, with, in addition, an amorphous carbon anode, which later work has shown to be possible.

Of the work with low-temperature electrolyte there is little more to be said. Moissan showed that copper is inert and anodically passive to fluorine, and Société Poulenc Freres et M. Meslans [8] patented a cell in which the platinum anode was attached to a copper cylinder, located centrally in a cylindrical cell and surrounded by a perforated copper diaphragm, which did not need to be electrically insulated from the anode. Thus they avoided the difficulty of sealing the anode into the anode compartment, in a manner which would retain its insulation value and resistance to fluorine. This cell arrangement, proposed as the basis for a manufacturing plant installation, has a very modern appearance, and was exhibited at the Exposition Universelle de Paris in 1900.

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[4] *Compt. rend.*, 1928, **181**, 917; P. Lebeau, *Bull. Soc. d'Encourag.*, 1927, **139**, 15.

[5] *Trans. Electrochem. Soc.*, 1934, **66**, 245.

[6] "Die Chemie des Fluors", Verlag Springer, Berlin, 1920.

[7] W. S. Calcott and A. F. Benning, U.S.P. 2,034,458 (1936).

[8] G.P. 129,825 (1902).

The early workers in this field laboured under more difficulties than the choice of electrolyte and anode. The raw material for their work was aqueous hydrofluoric acid, from which potassium acid fluoride was made and crystallised, dehydrated and then decomposed, by heating, to give the anhydrous acid. It was obviously an advantage of the high-temperature electrolyte that one stage of this preparation could be omitted, and then in the 'twenties supplies of the acid fluoride could be purchased, and the chemical side of the problem of making fluorine became much simpler. In the 'thirties supplies of anhydrous hydrogen fluoride also became available and the medium-temperature cell, with the possibility of electrolyte revivification from this source, was at no disadvantage.

Fluorine Cell Development from 1919 to 1939.—The studies on fluorine production by Mathers and his co-workers were required by the Chemical Warfare Service of the U.S. Government. A cell similar in form to that of Poulenc and Meslans was developed. The heavy copper containing vessel, 8 ins. deep, 3·5 ins. diameter, served as cathode and was externally electrically heated. The sheet-copper diaphragm, 2 in. in diameter, was slotted at the lower end and closed at the bottom. Inside the diaphragm was an Acheson graphite anode, suspended from a copper rod which was insulated from the diaphragm by a gland packed with powdered fluorspar, rammed hard. It was better to insulate the diaphragm, for some corrosion occurred when it was anodic. In starting a cell, only a low current could be passed. If too high a current density were applied, the cell quickly polarised, the current fell, and a potential of 50—60 volts was required to maintain the original current density. In these circumstances there was the appearance of a gas film round the anode, with small sparks through it (this is very similar to the well-known " anode effect " of fusion electrolysis). This effect was attributed to the presence of small amounts of water in the salt, and the formation of an oxygen film owing to its prior discharge. The phenomenon is constantly referred to by later workers. There is no explanation of how the oxygen discharge gives rise to the " gas film " and, as will be seen later, there is a very interesting field of study, still almost untouched, in the phenomena at fluorine–carbon anodes, especially in presence of small quantities of water.

Mathers electrolysed at a current density of 0·1—0·2 amp./sq. in. for several hours. During this period fluorine was not evolved, but when it began to appear, the current density could be increased to the normal working figure of 0·5—1·0 amp./sq. in. At 250°, the cell took 10 amps. at 15 volts. Some corrosion of the copper parts occurred, and copper fluoride thickened the melt, a process assisted by the deposition of potassium fluoride as the hydrogen fluoride content decreased. To some extent this process could be avoided by steadily increasing the temperature of electrolysis, but this, on the other hand, increased the rate of corrosion of the copper and the volatilisation of hydrogen fluoride and, above 300°, attack on the graphite anode became considerable. As the electrolyte became thicker, there was a tendency to frothing, and this led to electrolyte being carried into the outlet pipe and then solidifying. The fluorine was then forced under the diaphragm, mixed with the hydrogen, and caused explosions. It was not found possible to regenerate the electrolyte by passing in hydrogen fluoride, and therefore when the melting point of the electrolyte was up to about 280°, it was discarded and a fresh batch introduced. Mathers commented that it was remarkable that, in the years he was working with fluorine, Ruff did not discover this relatively simple method, and considered that there were no special difficulties in the manipulation of the apparatus. The problems indicated—sealing in the anode, polarisation, corrosion of the container, outlet-pipe blockage—are the main subjects of attention by subsequent workers.

Many cells of a very similar sort of size and capacity were introduced in the next twenty years. F. Meyer and W. Sandow [9] in 1921 took up a suggestion of Mathers and used as container artificial graphite. They had a special ribbed and club-shaped anode to reduce current density, and pre-electrolysed at a low current density. They investigated the effect of other fluorides in lowering the melting point of the electrolyte, but found the partial pressure of hydrogen fluoride was increased by any addition. There was some ozone in the anode gas in the early stages, but never more than 0·2% of carbon fluorides. Current efficiency was 75%. A cell of the Mathers pattern was used by W. R. Smythe [10] for study of the spectrum of fluorine. The hydrogen fluoride was removed by sodium fluoride, and the fluorine then had very little action on glass. J. Simons [11] in 1924 described a cell very similar to that of Mathers : he found Portland cement made an adequate anode seal, and the electrolyte was pre-electrolysed at low current density in an open cell until fluorine was evolved. Many workers used a cell of the Simons pattern in the next 15 years, in some cases monel metal being used in place of copper. S. F. Whearty, junr.,[12] used a cast magnesium body and an electrolyte containing 35% of sodium fluoride, and working at 170°. M. Bodenstein, H. Jokusch, and H. Krekeler [13] also used a magnesium alloy cell body but introduced the electrodes from below : the sealing in of the electrodes by solidified electrolyte was the subject of a patent assigned to I.G. Farbenindustrie.[14] A return to Moissan's cell type was shown by L. M. Dennis, J. M. Veeder, and E. G. Rochow,[15] who describe a V-shaped cell made of copper pipe, and several workers used this arrangement in copper or in nickel.

In 1925 Lebeau and Damiens introduced a cell using medium-temperature electrolyte, with a metal, preferably a nickel, anode. This was later to become the leading type. Several workers used this electrolyte, and its use by Cady [16] is noteworthy because it was the first case in which anhydrous hydrogen fluoride was obtained from a manufacturer and used for regeneration of the electrolyte *in situ*. This was in 1935.

[9] *Ber.*, 1921, **54**, 759.

[10] *Astrophys. J.*, 1921, **54**, 133.

[11] *J. Amer. Chem. Soc.*, 1924, **46**, 2175.

[12] *J. Physical Chem.*, 1931, **35**, 3121.

[13] *Chem. Fabr.*, 1935, **8**, 283.

[14] H. Krekeler, G.P. 522,885 (1931) ; 558,829 (1932).

[15] *J. Amer. Chem. Soc.*, 1931, **53**, 3263 ; L. M. Dennis and E. G. Rochow, *ibid.*, 1934, **56**, 879.

[16] *Ibid.*, 1935, **57**, 246.

An important study of factors affecting carbon anode behaviour was made by K. Fredenhagen and O. Krefft.[17] They dried their potassium bifluoride in a stream of dry air at an elevated temperature and tested for dryness by distilling off some hydrogen fluoride, which had to have a specific conductivity at 0° of less than 0·02 mho. In an electrolyte so prepared, a practically pure fluorine could be generated immediately at a graphite or amorphous carbon anode, and a reproducible current–voltage curve could be obtained. If water were added, polarisation occurred, and no reproducible curve could be obtained, until the water content exceeded 1%, but then the anode gas was oxygen. It was found also that for electrolytes with HF : KF ratio below 1·8, graphite was unwetted, and could then be used satisfactorily as an anode. Above this ratio (38·3% HF) wetting occurred and caused disintegration of the anode. Amorphous carbon anodes behaved similarly, but the limit at which wetting began was different—actually at a much higher hydrogen fluoride content. The use of anodes of graphite or carbon in an electrolyte which did not wet them was the basis of a patent claim by Fredenhagen.[18] Later papers by A. L. Henne[19] and Cady, D. A. Rogers, and C. A. Carlson[20] were not so clear as to when a graphite or carbon anode could be employed in medium-temperature electrolyte.

American Wartime Developments.—During the second world war, fluorine production was developed in U.S.A. in connection with the atom bomb, in Germany in connection with a wartime requirement for chlorine trifluoride. It is surprising that, although the principal interest in America before the war had been in high-temperature cells, yet the industrial developments were in medium-temperature cells, first with nickel anodes, later with carbon anodes;[21] and whilst it was German work which had principally pointed the way to the possibilities of the medium-temperature cell, wartime expansion there was of the high-temperature cell.[22]

In the American developments, cells of 1000—2000-amp. capacity with medium-temperature electrolyte were developed by Hooker Electrochemical Co., Harshaw Chemical Co., and E. I. du Pont de Nemours & Co. A large semi-technical installation of 600-amp. cells of high-temperature type is also described by Fowler *et al.*, and smaller installations, by Miller and McBee, of medium-temperature cells. A detailed account of the du Pont cell will be given, as representative: the work on this, especially in connection with nickel anodes, has been described in considerable detail by R. C. Downing.[23] The original choice of the medium-temperature electrolyte using nickel anodes might be questioned, but comparing the position as now known, when carbon anodes have successfully replaced nickel, there can be

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[17] *Z. Elektrochem.*, 1929, **35**, 670.

[18] G.P. 493,873 (1930); 511,808 (1930).

[19] *J. Amer. Chem. Soc.*, 1938, **60**, 96.

[20] *Ind. Eng. Chem.*, 1942, **34**, 443.

[21] For a full account of American wartime developments, see various papers, *ibid.*, 1947, **39** (March).

[22] German work in the fluorine field is fully described in B.I.O.S. 1595; see also H. R. Neumark, *Trans. Electrochem. Soc.*, 1946, **91**, preprint 3; and B.I.O.S. 72; 261; C.I.O.S. XXII—17; 22/XXIX—14; F.I.A.T. 838; P.B. 6641.

[23] P.B. 60796.

little doubt that this gives the most economical arrangement. The corrosion is very much less than in high-temperature electrolyte, mild steel may be employed for cell construction, the control of a temperature of about 100° is much simpler than one about 250°, and the anodic polarisation tendency is less pronounced. Fluorine manufacture was started with large numbers of nickel anode cells, but the current efficiency was low, about 70%, the nickel consumption heavy, and electrolyte conditioning, to remove nickel fluorides, was a very big job. Downing states that the sludge contains NiF_3,KF. A fluoride of tervalent nickel has not been previously reported. The cells were all finally converted to carbon anodes. The cells had a rectangular steel container, about 4 ft. long, $2\frac{3}{4}$ ft. deep, $1\frac{1}{3}$ ft. wide, provided with a jacket for circulating water to maintain optimum temperature conditions. The steel cover carried electrodes and diaphragms in rows along the length. There were two rows of anodes, built up each of six carbon plates side by side. Each plate was 18 ins. long, $6\frac{1}{4}$ ins. wide, $1\frac{1}{4}$ ins. thick. To each row of anodes there was a double row of sheet-steel cathodes, and between the facing electrodes was a diaphragm, solid metal in the gas space, perforated monel metal sheet in the electrolyte. The anodes were bolted to copper carriers, and these supported by copper rods which passed through stuffing boxes in the cover. The stuffing box was made gas-tight, and electrical insulation provided, by rings of " Teflon ", the solid polymer of tetrafluoroethylene which was itself a wartime discovery.[24] This is a hard, horny material, inert to all reagents, including even fluorine under ordinary conditions, electrically non-conducting, and solid up to at least 300° The cathode was similarly supported and insulated. The cover was provided with gas-outlet connections, and a pipe for hydrogen fluoride addition provided. This cell took about 1500 amps. at a voltage of 8·5 at the start, gradually deteriorating to 11·0. The working temperature was in the range 95—115°, the current density was 0·5 amp./sq. in., the current efficiency more than 90%, the anode gas contained 5—15% of hydrogen fluoride, and on a hydrogen fluoride-free basis the fluorine content was greater than 98%, with a trace of fluorine oxide, F_2O.

If it had not been found possible to use carbon anodes, the very heavy consumption of nickel, and expensive electrolyte regeneration operations, would probably have made the high-temperature cell, with a graphite anode, more economic. The work of Fredenhagen and Krefft had indicated clearly the controlling factors, although they had suggested a composition between KF,HF and KF,1·6HF when graphite could be employed, and a temperature at the start of 160°. With this composition at this temperature the hydrogen fluoride vapour pressure is high, and the generally favourable conditions (low corrosion, ease of control) associated with a lower temperature and higher HF proportion (up to KF,2·2HF) are beginning to disappear. In this most favourable range, it was never found possible to employ graphite, but amorphous carbon was satisfactorily used.

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[24] E. B. Yelton, *Chem. Eng.*, 1947, **54,** No. 3, 264 ; *Chem. Met. Eng.*, 1946, **53,** No. 4, 145.

The cells still showed a tendency to polarisation, which has several possible origins, as follows.

(1) The electrical contact to the anode could deteriorate, and indeed it has been suggested that the provision of a permanently satisfactory connection is one of the remaining outstanding problems. The gradual increase of the voltage from 8·5 at the start to 11·0 or more was largely caused by this deterioration.

(2) Water in the electrolyte exerted its known effect. Each cell was provided with a subsidiary nickel anode, which carried all the current at the start, and the anode gas was mainly oxygen. When the anode gas had reached a certain fluorine content, the carbon anodes were switched in. Accumulation of water (from the make-up hydrogen fluoride) might occur, and some use of the nickel anode might be necessary again during the course of operation. Downing says that there was some other unexplained effect of this electrolysis at a nickel anode, in addition to its effect in removing water.

(3) Low hydrogen fluoride concentration could sometimes cause polarisation. It is suggested that 37·5% of hydrogen fluoride, equivalent to KF,1·75HF, was a limiting figure and that in this case the voltage rise occurred at the cathode. Normally the bulk of the voltage drop occurs at the anode. This difficulty was immediately cured by addition of acid, the preferred range of acid content being 38—40%.

(4) Polarisation could still occur, not attributable to any of the above effects: it was called "gas film" polarisation, and attributed to non-wetting of the carbon anodes by the electrolyte. Pinkston states that the anodes were not wetted by the electrolyte, and when removed from the liquid they were clean and black. This is a repetition of the observation by Cady,[20] who further stated that such anodes were not wetted by tap water, but carbon cathodes in the same electrolyte did not become non-wetting. It was found that this difficulty was minimised by the addition of 1—2% of lithium fluoride to the electrolyte; this addition was made in the first place in an attempt to lower the melting point of the electrolyte, and the Harshaw workers observed this other effect of the addition. Schumb, on the other hand, states that the lithium fluoride was insoluble and tended to settle out, but if the mud at the bottom of the cell was stirred up, there was a temporary improvement of the cell performance, as regards polarisation tendency. Aluminium fluoride had a similar effect and equally tended to settle out. The addition of 1—2% of lithium fluoride became standard practice in the American industrial installations, and has been the subject of a patent.[25]

Downing states that the two discoveries which eliminated polarisation as an obstacle to the commercial operation of carbon anode cells were the addition of lithium fluoride to the electrolyte, and the conditioning of the electrolyte by operating with a nickel anode. The carbon anodes used in these cells were of a special character. The du Pont cell had a carbon especially strengthened by impregnation with carbonaceous material and

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[25] W. C. Schumb and A. J. Stevens, U.S.P. 2,422,590 (1943).

rebaking, and the Harshaw cell had a carbon rod impregnated with copper : the latter was stronger, permitted better electrical connection being made, and was not so sensitive to acid concentration.

It may be said that all this American work solved very satisfactorily the problem of making fluorine on a large scale, but left unsolved the interesting theoretical problem of the behaviour of carbon anodes. In low-temperature electrolyte, graphite almost immediately on being rendered anodic swells and disintegrates, a behaviour which persists until the electrolyte composition reaches that of medium-temperature electrolyte ; even then polarisation is so severe as to render graphite unusable. Graphite anodes may be employed in high-temperature electrolyte, but even then there is a gradual deterioration. Amorphous carbon, completely polarised if not disintegrated in low-temperature electrolyte, may be satisfactorily employed (but with some limitations) in medium- and in high-temperature electrolyte. Precisely what is the relation to these phenomena of the behaviour attributed to water in the electrolyte, and its own intense polarising influence, is unexplained. Would polarisation (and disintegration ?) disappear if rigidly water-free systems were employed ? How does oxygen evolution cause such intense polarisation ? A further unusual phenomenon is the method of evolution of the fluorine itself, which A. J. Rudge, W. N. Howell, and H. Hill [26] have related to the high angle of wetting at the anode, but which requires further study, and which may cast an interesting light on the puzzling " anode effect " observed in fusion electrolyses.

An interesting feature of the Pennsylvania Salt Mfg. Co.'s cell, described by J. F. Gall and H. C. Miller [27] and by R. W. Porter [28] was that no diaphragm was interposed between the electrodes, only a gas barrier immersed to a depth of 2 in. to divide anode from cathode gas. The high-temperature cell described by Fowler seems a very practical equipment, but requires monel construction instead of steel, and corrosion was appreciable in places : polarisation seems to have been a recurrent phenomenon and the graphite anodes had a restricted life. Regeneration of the electrolyte with hydrogen fluoride vapour was possible, and the cell worked at an anodic current density of 300 amps. per sq. ft.—four times that of medium-temperature cells—so that a more compact installation was possible.

German Wartime Developments.—Two German cells developed during the war are worthy of attention. I.G. Farbenindustrie developed, for experimental purposes only, a cell of medium-temperature type at their research laboratories at Leverkusen. They had developed a 250-amp. cell by 1940, and a 2000-amp. cell by 1942. The construction was in magnesium alloy, with hard-carbon anodes, impregnated and re-baked, and magnesium sheet cathodes. There was no diaphragm, only a gas-separating barrier. The 2000-amp. cell was long and narrow (10 ft. long, 1·6 ft. wide and deep) and had external electrolyte circulation and cooling. The electrolyte contained about 46% of hydrogen fluoride (KF,2·5HF), the working temperature was 75—85°, and in these conditions, even when hydrogen fluoride containing

[26] *Nature*, 1947, **160**, 504.

[27] *Ind. Eng. Chem.*, 1947, **39**, 262.

[28] *Chem. Eng.*, 1948, **55**, No. 4, 102.

2—3% of water was used for make-up, no trouble was experienced with polarisation. This seems to require further examination.

A fluorine plant was erected at Falkenhagen, near Berlin, to make 720 tons per annum of fluorine, for conversion into chlorine trifluoride. This plant, using high-temperature electrolyte, was apparently under the direct control of the German High Command. There had obviously been a good deal of study of fluorine production on which the design of the cell was based, but it is not known what the antecedents of this plant were. It is indeed noteworthy that the I.G. cell was not developed on a manufacturing scale for this plant. The O.K.H. cell (Ober Kommando des Heeres) had a capacity of 2000—2500 amps. and was made in magnesium alloy, with graphite anodes and silver cathodes ; each electrode was sealed into a diaphragm bell of magnesium alloy, slotted in the area where the electrodes were facing each other. Each cell stood on its own weighing machine, to control the hydrogen fluoride input, and was provided with its own rectifier for D.C. supply. Great stress was laid on the purity of the electrolyte, and of the make-up hydrogen fluoride ; water and sulphur oxides must be completely removed, but some hydrofluorosilicic acid (up to 3% in the electrolyte) was permissible. The electrolyte was purified by pre-electrolysis, before being charged into the cell, which had then to be operated for an hour at 30—60 volts, to condition the anodes, before it was installed in its normal working position.

The acid for cell make-up was purified by passage with 1—2% of fluorine through a nickel reactor at 300°. This acid, after condensation, was re-vaporised for addition to the cell, the addition being controlled by the weight of the cell, and a catharometric record of the hydrogen fluoride in the cathodic hydrogen. The cell operated between 245° and 253°, the starting voltage was 6·0—6·5, which gradually rose, over a period of 3 months, to 11·5 : a heavy load of up to 5000 amps. was then applied for 5—10 minutes, when normal operation was recommenced, the voltage returning to the initial figure. The anodic current density was 60—70 amps. per sq. ft., which was very similar to American medium-temperature practice and very different from the very high values at which Fowler's cell ran. A current efficiency greater than 90% was obtained. Some corrosion of the silver cathode, and the magnesium parts, occurred, so that after a year or so the electrolyte was emptied from the cell to remove accumulated sludge. The total life of the anode is stated to have been 12 months, but the reason for the termination of anode life is not given.

A good deal of interesting work appears to have been done in connection with this cell development, and some of it has been reported by Neumark. The absorption of fluorine on graphite and the formation of complex intercalation compounds, is described, and it is suggested that this accounts for the gradual deterioration of the cell voltage. The fluorides of rubidium and cæsium were also studied as possible alternatives to potassium, and the conclusion reached that no advantage was to be observed. Kwasnik, on the other hand, states that they would be preferred, in the I.G. cell, were it not for their high price and scarcity.

Chemical Production of Fluorine.—Perhaps a word should be said with regard to the attempted chemical production of fluorine. This was of course studied from Davy onwards, and he was well aware of the difficulty he would have in finding vessels which would withstand fluorine at the high temperatures presumably necessary. Platinum and gold are not particularly good in this connection. Brauner was reported to have been successful in making fluorine in 1882 by thermal decomposition of the tetrafluorides of lead and cerium, but in 1916 O. Ruff [29] cast doubt on this and B. Brauner [30] agreed with him. The studies which produced the Mathers cell also embraced chemical preparations, and G. L. Clark [31] describes methods of preparing complex salts such as $3KF,HF,PbF_4$ and Na_2PbF_8 : the former loses hydrogen fluoride at 250° and evolves fluorine at 300°, and the latter may decompose at 250°. The studies of K. Jellinek and A. Rudat [32] on the reducibility of fluorides by hydrogen are interesting and show very high heats of formation, *e.g.*, for FeF_3.

A patent for the production of fluorine by action of oxygen on the oxyfluorides of titanium, zirconium, or hafnium was taken out in 1926.[33] The difluoride of silver, AgF_2, was first reported by M. S. Ebert, E. L. Rodowskas, and J. C. W. Frazer in 1933,[34] and it is suggested,[35] without confirmation, that the equilibrium pressure of fluorine over this salt reaches 1 atmosphere at about 450°. It is probable that with increasing knowledge of materials resistant to fluorine, it would be possible to find a fluoride which would evolve fluorine on heating, and this may be a means of generating very pure fluorine. During the war, very considerable use was made in America of fluorine carriers, especially cobalt trifluoride, for fluorinating hydrocarbons. In addition AgF_2, MnF_3, CeF_4, PbF_4, HgF_2, and others were studied. These higher fluorides were made by treatment of lower-valency compounds with electrolytically produced fluorine, and it is probable that this method of applying fluorine may undergo further development.

Handling of Fluorine.—Considerable confusion and misapprehension have been prevalent with regard to the difficulties of working with fluorine. It reacts fairly readily with many organic materials such as rubber and textiles and with moisture : the hydrogen fluoride present in gas direct from the cell reacts, of course, with glass ; but after removal of this hydrogen fluoride, fluorine can be handled readily in glass, harder glasses being more resistant and silica excellent.[36] Dry metals also are resistant. Thus pure fluorine free from hydrogen fluoride, out of contact with rubber, is quite inert in glass or metal equipment. For connections, especially in metal, pressure or force joints as commonly used in domestic plumbing, and used by Henne [19] for making connection to his cell, are very useful. For stopcock lubricants,

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[29] *Z. anorg. Chem.*, 1916, **98**, 27.

[30] *Ibid.*, p., 38.

[31] *J. Amer. Chem. Soc.*, 1919, **41**, 1477.

[32] *Z. anorg. Chem.*, 1928, **175**, 281.

[33] N. V. Phillips Gloeilampenfabrikien, B.P. 262,918 (1926).

[34] *J. Amer. Chem. Soc.*, 1933, **55**, 3056.

[35] O. Ruff and M. Giese, *Z. anorg. Chem.*, 1934, **219**, 143.

[36] S. Aoyama and A. Kanda, *Bull. Chem. Soc. Japan*, 1937, **12**, 409.

material of the fluorocarbon type is desirable, and this at present is not available commercially.

For removing hydrogen fluoride, the cooling possible with solid carbon dioxide is inadequate, for the vapour pressure is still appreciable at −60°. If cooling is to be resorted to, liquid air must be used. A better method is the use of sodium or potassium fluoride as absorbents, as first used by Moissan. The former is preferred, as it does not give any liquid products which may cause blockages in the apparatus. These have been generally used by fluorine workers, and the sodium fluoride is preferably used in a granular or pelleted form. Data on the effect of cooling, and of sodium fluoride absorption, in removing hydrogen fluoride, have been given by the du Pont workers.[21] Porter [28] describes how sodium fluoride absorbers are regenerated *in situ* by heating. At the O.K.H. plant in Germany, potassium fluoride was used and liquid products drained off. Even at temperatures up to 100° at least, mild steel, copper, nickel, monel, aluminium, magnesium, and brass are practically completely inert to fluorine and there is no need to use platinum. At higher temperatures platinum is not very good : nickel or monel is best, being useful even at 600°.[21, 37] Soft metals, lead and tin, are not resistant and soldering cannot be used. Amongst non-metallic materials, sintered alumina, now becoming commercially available, is resistant up to at least 700°,[38] and there is no need to go to the specially made fluorspar or fluoride porcelains described by Damiens [39] and by O. Ruff and A. Riebeth.[40]

Fluorine compression is not very easy mechanically, although it has been done up to 40 lbs./sq. in.[21] For higher pressures the gas is liquefied by cooling with liquid air or nitrogen and then allowed to evaporate under pressure into a suitable container. H. von Wartenberg [41] has referred to the use of a cylinder containing fluorine at 2000 lbs./sq. in., supplied to him by I.G. Farbenindustrie before the war, and I.G. practice has been described.[22] Gas compressed to 400 lbs./sq. in. was apparently used in America during the war, but only under stringent precautions. A trace of grease or other organic matter could react violently and cause such a local high temperature as to set the metal of the valve burning : leakage through the packing of the gland could have the same effect. Containers of compressed fluorine were therefore stored behind heavy steel or thick brick walls, and valves manipulated by remote control. In the light of this it seems improbable that compressed fluorine is ever likely to become an article of commerce.

In the liquefaction and re-evaporation of fluorine, Ruff and O. Bretschneider [42] pointed out that explosive compounds of an unknown character, possibly $ClOF$ or O_3, accumulate in the less volatile residues. Both I.G. Farbenindustrie and Penn. Salt follow Ruff's advice and heat the fluorine to 300°, to decompose these impurities, before liquefying it.

[37] W. R. Myers and W. B. deLong, *Chem. Eng. Progress*, 1948, **44**, 359.

[38] O. Hannebohn and W. Klemm, *Z. anorg. Chem.*, 1936, **229**, 336.

[39] *Compt. rend.*, 1931, **192**, 1235 ; A. Damiens and L. Domange, *ibid.*, p. 1711.

[40] *Z. anorg. Chem.*, 1928, **173**, 373.

[41] *Ibid.*, 1939, **242**, 406 ; 1941, **247**, 135.

[42] *Ibid.*, 1934, **217**, 1.

Anhydrous Hydrogen Fluoride.—Moissan's procedure for making his anhydrous liquid has already been described. The thermal decomposition of acid potassium fluoride, and the conditions required for production of acid of low moisture content, have been studied by K. Fredenhagen and G. Cadenbach ;[43] and although on a small scale fluorine cell workers were content to purchase the acid fluoride and discard it when partly exhausted, yet for large-scale manufacture a supply of anhydrous acid was essential for both medium-temperature and high-temperature cells.

A demand for anhydrous hydrogen fluoride (" AHF ") in industry first developed about 1930 in the U.S.A for the manufacture of the chlorofluoromethanes, the " Freons ".[44] About 10 years later a further demand developed, also in the U.S.A., for the use of this acid as alkylation catalyst for producing aviation petrol in the petroleum industry. The American wartime fluorine industry thus found the plant in existence to supply its raw materials. Production of some 25,000 tons of AHF was estimated in 1944. In Germany, a special plant was built in Bavaria to supply the O.K.H. plant, although I.G. also had an AHF plant at Leverkusen.

The method of manufacture is by the action of concentrated sulphuric acid on fluorspar at a temperature of about 250°. The fluorspar should be high grade, may have been subjected to a flotation process to remove impurities, should be low in silica, galena, and moisture, and have a minimum of 98—99% CaF_2 content. It is finely ground, dried, mixed with acid, and fed into the reaction vessel. Penn. Salt in their plant at Cornwell Heights use a rotary kiln, externally gas fired, and the acid is absorbed in weaker aqueous solution to give an 80% solution which is fractionally distilled to give an anhydrous acid and a weaker solution returned to the absorption system. The plant at Stulln, Bavaria, with a capacity of 3000 tons of AHF per annum, uses a stationary retort, the acid–spar mixture being forced through by slow paddle agitators. The acid is condensed by cooling, to give a product with 10% of water, which is batch-distilled through fractionating columns to give a pure anhydrous acid. The I.G. plant, with a capacity of 10,000 tons per annum, used rotary kilns of steel plate, brick-lined : the acid is condensed by cooling, and the crude product contains 5% of water, but a purer product is obtainable by separately collecting the condensate from the final condenser in the series.

Some Recent Developments in Fluorine Compounds.—Finally, it is of interest to draw attention to developments in the field of fluorine compounds, more particularly those involving elementary fluorine in their production. Hence we will not refer further to developments in recent years of boron trifluoride and fluoroborates, of the chlorofluoro-derivatives of methane and ethane, such as CF_2Cl_2, which have become known generally under their trade name of " Freons ", or to the polymers of tetrafluoroethylene and chlorotrifluoroethylene.

The most outstanding developments of recent years have been in the field of the fluorocarbons. Carbon tetrafluoride was very incorrectly

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[43] *Ibid.*, 1929, **178**, 289.

[44] J. R. Callahan, *Chem. Met. Eng.*, 1945, **52**, 94.

described by Moissan [45] and only properly identified by Lebeau and Damiens in 1926.[46] It is a gas, liquefied at atmospheric pressure at − 128°, stable and chemically inert, unattacked by most reagents. Ruff and R. Keim [47] in 1930 and Ruff and Bretschneider in 1934 [42] described a number of fluorocarbons formed by the action of fluorine on carbon, up to C_5F_{12}, and J. H. Simons and L. P. Block [48] went up to C_7F_{14}. These compounds, analogues of the hydrocarbons, are all stable and inert, and above the butane derivatives actually have boiling points lower than the corresponding hydrocarbon. In addition, at temperatures below about 400°, Ruff and Bretschneider showed that different forms of carbon give rise to a solid monofluoride $(CF)_n$, apparently formed by intercalation of fluorine molecules between the layer planes of the graphite crystallites. It is a chemically inert compound which, however, decomposes above 400° into carbon tetrafluoride and higher fluorocarbons ; in presence of fluorine, particularly, this decomposition occurs explosively.

The American wartime fluorine cell developments were largely for the production of fluorocarbons. Two types of compound were required, a volatile liquid and a lubricating material ; for the former perfluorodimethyl*cyclo*hexane $C_6F_{10}(CF_3)_2$ was made, for the latter, various types of hydrocarbon, or chlorohydrocarbon, were fluorinated. A very wide range of fluoro-compounds was made, both of aliphatic and polycyclic character, mostly saturated. McBee [21] has described the production of perfluorobenzene, C_6F_6, but says very little regarding its properties. It is a liquid, b.p. 81—82°. The properties of these compounds have been described by Fowler and by Cady and Grosse.[21] A variety of methods of preparation was employed. The direct fluorination of hydrocarbons with fluorine over a silver–copper catalyst is described by Cady, but in general the process used a fluorine carrier of the type of cobalt trifluoride. In many cases hydrocarbon materials were chlorinated, and the chlorine replaced with fluorine by treatment with hydrogen fluoride or other agent, before completion of the substitution, and saturation, in the above way.

Sulphur hexafluoride was made in 1900 by Moissan and Lebeau by burning sulphur in fluorine, and can still only be made by this or a related method. It has a very high electrical breakdown capacity, and this, combined with its low boiling point, has made it particularly suitable for filling the Van de Graaff high-voltage generator.[49] The production of sulphur hexafluoride on a laboratory scale has been described by Schumb,[21] and on a technical scale by Porter.[28] The initial product of combustion is contaminated with lower fluorides, with the highly toxic S_2F_{10}, and with hydrogen fluoride. After an alkaline wash, the gases are passed through a heated metal tube to decompose other impurities, again alkali-washed before drying, and compressing into cylinders.

The chlorine fluorides were only discovered some twenty years ago, and

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[45] *Compt. rend.*, 1890, **110,** 951.

[46] *Ibid.*, 1926, **182,** 1340 ; 1930, **191,** 939.

[47] *Z. anorg. Chem.*, 1930, **192,** 249

[48] *J. Amer. Chem. Soc.*, 1939, **61,** 2962.

[49] W. W. Buechner, R. J. Van de Graaff, A. Sperduto, L. R. Macintosh, and E. A. Burrill, *Rev. Sci. Instr.*, 1947, **18,** 754.

during the war the trifluoride especially underwent some development. Ruff *et al.*[50] in 1928 reported that the action of fluorine on hydrogen chloride at liquid-air temperature led to the formation of chlorine monofluoride, boiling at − 103°. K. Fredenhagen and O. Krefft [51] showed that an equimolecular mixture of fluorine and chlorine exploded on sparking, and Ruff [52] stated that fluorine readily burns in chlorine. Then in 1930 Ruff and H. Krug [53] showed that fluorine and chlorine, mixed in the proportion of 1 : 3, combined gently when heated to about 300° to give the trifluoride, ClF_3, b.p. 11·3°. This is a very reactive material, in many reactions similar to fluorine itself. Little work has been reported on these compounds.

The fluorine made in the O.K.H. cells at Falkenhagen was entirely converted into chlorine trifluoride, which was to be employed, apparently, as an incendiary agent in a manner not clearly indicated. The very violent reaction which chlorine trifluoride shows with water and organic matter would appear to make it fairly effective for incendiary purposes, whilst, like fluorine itself, it can readily be handled in steel or other metal equipment ; and unlike bottled fluorine, chlorine trifluoride does not develop a high pressure in containers, and there is therefore not the same risk of uncontrollable escape. In the manufacturing process described, fluorine from the cells is mixed with three times its volume of chlorine in stages : in the first stage, on heating to 200°, the monofluoride is formed, and finally the trifluoride is formed at 250—280°. The reaction vessels are nickel throughout, with shell-and-tube heat exchangers cooled with air when the reaction is proceeding normally The chlorine trifluoride is condensed out by cooling, and stored in steel vessels of 5 m.^{3} capacity. The efficiency of conversion of fluorine into the trifluoride is 95%. Chlorine trifluoride is also stated to be one of the products made from the fluorine from the Pennsylvania Salt Mfg. Co.'s cell already described,[28] by a process similar to the German. It is stated that, under controlled conditions, reaction of chlorine trifluoride with organic compounds leads to the introduction of both fluorine and chlorine into the organic molecule.

The possibility of using higher fluorides such as cobalt trifluoride as fluorine carriers had been proposed before the war by Ruff. The American fluorocarbon production led to a very considerable development of this technique, and, *e.g.*, Fowler has considered the various fluorides which may be used. Cobalt trifluoride was principally used, manganese trifluoride and silver difluoride to a less extent, the latter largely by McBee and his school. These higher fluorides are relatively stable compounds in themselves, made by the action of fluorine at somewhat elevated temperatures (200—400°) on lower fluorides, or chlorides. They yield up their fluorine in a controlled manner, to organic materials in the liquid or the vapour state, at temperatures from 150° to 400°. These compounds may find many uses for laboratories whose fluorine requirements hardly justify the installation of a fluorine cell, and their post-war production has been referred to by Porter.[28]

[50] O. Ruff, E. Ascher, J. Fischer, and F. Laass, *Z. anorg. Chem.*, 1928, **176**, 258.

[51] *Z. physikal. Chem.*, 1929, **141**, 221.

[52] *Z. angew. Chem.*, 1929, **42**, 807.

[53] *Z. anorg. Chem.*, 1930, **190**, 270.